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•634 AJL
10/17-RC

B36 PART 7 Pp. 1525–1732 15 JULY 1980

Acta Crystallographica

...ATIONAL UNION OF CRYSTALLOGRAPHY
...ARD, International Booksellers and Publishers Ltd, Copenhagen

...525–1732 (1980) ISSN 0567-7408

Les auteurs remercient Mlle José Piquion du Laboratoire de Chimie Organique de la Faculté des Sciences d'Abidjan qui a extrait ce composé; la Direction de l'Office Central de Mécanographie d'Abidjan (Côte d'Ivoire) qui nous a permis d'effectuer les calculs sur ses ordinateurs IBM 370-145. L'un de nous (JPD) remercie le Fonds National de la Recherche Scientifique pour le mandat dont il a bénéficié.

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The Structure of Acetylated Napoleogenin

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(*Received* 18 *October* 1979; *accepted* 11 *February* 1980)

Abstract

Acetylated napoleogenin, $C_{58}H_{84}O_{18}$, crystallizes in space group $P2_1$ with two molecules in a unit cell of dimensions $a = 19{\cdot}127\ (1)$, $b = 10{\cdot}812\ (1)$, $c = 14{\cdot}879\ (1)$ Å, $\beta = 102{\cdot}540\ (2)°$. The crystal structure was solved by direct methods. Full-matrix least-squares refinement with all atoms treated isotropically and using 3139 reflections gave an R value of 0·108. The compound possesses a triterpene skeleton with *cis*-fused D and E rings in the chair form. A 3,4-di-*O*-angelyl-6-deoxy-β-glucopyranosyl group sits at C(21) on the E ring. The molecular structure of acetylated napoleogenin is formulated by the present analysis as 21β-(2-*O*-acetyl-3,4-di-*O*-angelyl-6-deoxy-β-glucopyranosyloxy)-3β,16α,22α,24,28-pentaacetoxy-olean-12-ene. The large distortion of the whole molecular skeleton may result from 1,3 diaxial interaction. The packing is mainly dictated by close van der Waals contacts between the molecules.

Introduction

Within the framework of chemical taxonomy studies, the acetylated form of napoleogenin, a new pentacyclic

0567-7408/80/071593-06$01.00

triterpene, was isolated from the seeds of *Napoleonaea imperialis*, a plant native to Zaïre. An X-ray crystal-structure investigation of the compound was undertaken in order to establish unequivocally its chemical structure and stereochemistry.

Table 1. *Atomic positional and isotropic thermal parameters with standard deviations in acetylated napoleogenin*

	x	*y*	*z*	*B* (Å²)
(i) Triterpene nucleus				
C(1)	0·5868 (7)	0·047 (1)	−0·0589 (9)	6·3 (3)
C(2)	0·5595 (8)	0·063 (2)	−0·164 (1)	7·2 (3)
C(3)	0·6094 (7)	−0·002 (2)	−0·214 (1)	6·1 (3)
C(4)	0·6195 (7)	−0·142 (2)	−0·1966 (9)	5·9 (3)
C(5)	0·6442 (6)	−0·159 (1)	−0·1917 (8)	5·1 (2)
C(6)	0·6609 (6)	−0·290 (1)	−0·0571 (8)	4·8 (2)
C(7)	0·7072 (7)	−0·287 (1)	0·0403 (9)	5·5 (3)
C(8)	0·6706 (6)	−0·222 (1)	0·1111 (7)	4·4 (2)
C(9)	0·6418 (6)	−0·094 (1)	0·0712 (7)	4·4 (2)
C(10)	0·5957 (6)	−0·096 (1)	−0·0314 (8)	4·8 (2)
C(11)	0·6039 (7)	−0·027 (2)	0·136 (1)	6·8 (3)
C(12)	0·6383 (7)	−0·045 (2)	0·2365 (9)	5·7 (3)
C(13)	0·6943 (6)	−0·124 (1)	0·2691 (8)	4·8 (2)
C(14)	0·7283 (6)	−0·196 (1)	0·2040 (7)	4·3 (2)
C(15)	0·7571 (6)	−0·319 (1)	0·2482 (8)	5·1 (2)
C(16)	0·7920 (6)	−0·319 (1)	0·3532 (8)	4·7 (2)
C(17)	0·7468 (6)	−0·253 (1)	0·4107 (7)	4·4 (2)
C(18)	0·7208 (6)	−0·124 (1)	0·3740 (8)	4·4 (2)
C(19)	0·7756 (5)	−0·022 (1)	0·4064 (7)	4·4 (2)
C(20)	0·8003 (6)	−0·010 (1)	0·5115 (8)	4·6 (2)
C(21)	0·8372 (5)	−0·137 (1)	0·5414 (7)	3·8 (2)
C(22)	0·7860 (6)	−0·242 (1)	0·5156 (7)	4·5 (2)
(ii) Extranuclear				
C(23)	0·6816 (9)	−0·188 (2)	−0·241 (1)	8·0 (4)
C(24)	0·5513 (7)	−0·207 (1)	−0·244 (1)	6·2 (3)
C(25)	0·5199 (8)	−0·150 (2)	−0·042 (1)	6·8 (3)
C(26)	0·6107 (7)	−0·301 (2)	0·1299 (9)	5·8 (3)
C(27)	0·7924 (6)	−0·117 (1)	0·1880 (8)	5·2 (2)
C(28)	0·6778 (6)	−0·329 (1)	0·4023 (8)	5·1 (2)
C(29)	0·8561 (7)	0·095 (2)	0·531 (1)	6·0 (3)
C(30)	0·7390 (7)	0·020 (2)	0·5577 (9)	5·7 (3)
C(31)	0·5960 (9)	0·132 (2)	−0·348 (1)	7·7 (4)
C(32)	0·553 (1)	0·139 (2)	−0·445 (2)	10·5 (6)
C(33)	0·523 (1)	−0·422 (2)	−0·291 (1)	8·5 (4)
C(34)	0·549 (1)	−0·545 (2)	−0·281 (2)	10·6 (5)
C(35)	0·9223 (7)	−0·314 (2)	0·3678 (9)	5·9 (3)
C(36)	0·983 (1)	−0·231 (2)	0·379 (1)	9·0 (4)
C(37)	0·6493 (9)	−0·545 (2)	0·401 (1)	8·4 (4)
C(38)	0·673 (1)	−0·665 (2)	0·439 (2)	10·7 (5)
C(39)	0·8109 (8)	−0·430 (2)	0·606 (1)	6·9 (3)
C(40)	0·866 (1)	−0·536 (2)	0·617 (1)	9·5 (5)
O(1)	0·5805 (6)	0·018 (1)	−0·3126 (7)	7·7 (2)
O(2)	0·6359 (7)	0·200 (2)	−0·3110 (9)	10·2 (3)
O(3)	0·5631 (6)	−0·340 (1)	−0·2356 (7)	7·5 (2)
O(4)	0·4668 (8)	−0·378 (2)	−0·343 (1)	11·5 (4)
O(5)	0·8612 (4)	−0·252 (1)	0·3665 (5)	4·3 (1)
O(6)	0·9218 (5)	−0·426 (1)	0·3673 (7)	7·7 (2)
O(7)	0·6974 (5)	−0·458 (1)	0·4258 (6)	5·8 (2)
O(8)	0·597 (1)	−0·517 (2)	0·332 (1)	15·3 (5)
O(9)	0·8288 (4)	−0·353 (1)	0·5383 (5)	5·0 (2)
O(10)	0·7681 (7)	−0·412 (1)	0·6413 (8)	9·0 (3)
O(11)	0·8596 (4)	−0·138 (1)	0·6416 (5)	4·5 (1)

Table 1 (*cont.*)

	x	*y*	*z*	*B* (Å²)
(iii) Glucopyranosyl moiety				
C(1′)	0·9320 (6)	−0·128 (1)	0·6775 (7)	4·3 (2)
C(2′)	0·9452 (6)	−0·079 (1)	0·7747 (8)	4·5 (2)
C(3′)	1·0269 (5)	−0·072 (1)	0·8153 (8)	4·7 (2)
C(4′)	1·0603 (6)	−0·192 (1)	0·8042 (8)	4·7 (2)
C(5′)	1·0391 (7)	−0·240 (1)	0·7026 (9)	5·6 (2)
O(1′)	0·9637 (4)	−0·247 (1)	0·6774 (5)	4·7 (1)
C(6′)	1·0692 (8)	−0·370 (2)	0·691 (1)	6·4 (3)
C(7′)	1·1814 (8)	−0·212 (2)	0·897 (1)	6·4 (3)
C(8′)	1·260 (1)	−0·187 (2)	0·893 (1)	8·2 (4)
C(9′)	1·301 (1)	−0·156 (3)	0·977 (2)	11·2 (6)
C(10′)	1·2873 (7)	−0·142 (2)	1·0605 (9)	9·1 (3)
C(11′)	1·279 (1)	−0·192 (3)	0·798 (2)	11·2 (7)
C(7″)	1·0759 (8)	0·047 (2)	0·948 (1)	6·5 (3)
C(8″)	1·078 (1)	0·061 (2)	1·053 (1)	8·8 (3)
C(9″)	1·0416 (7)	0·015 (2)	1·0960 (9)	8·0 (3)
C(10″)	0·9722 (7)	−0·058 (2)	1·0686 (9)	9·1 (3)
C(11″)	1·142 (1)	0·149 (2)	1·093 (1)	8·8 (3)
C(12′)	0·8652 (7)	0·064 (2)	0·817 (1)	6·5 (3)
C(13′)	0·840 (1)	0·196 (2)	0·807 (1)	8·8 (4)
O(2′)	1·1383 (4)	−0·172 (1)	0·8199 (5)	5·6 (2)
O(3′)	1·1558 (8)	−0·258 (2)	0·956 (1)	11·0 (4)
O(2″)	1·0318 (4)	−0·051 (1)	0·9124 (6)	5·6 (2)
O(3″)	1·1033 (8)	0·116 (2)	0·907 (1)	10·0 (3)
O(4′)	0·9187 (4)	0·044 (1)	0·7743 (5)	5·4 (2)
O(5′)	0·8376 (6)	−0·014 (1)	0·8567 (9)	8·9 (3)

Experimental

Colorless needle-shaped crystals, elongated along the [illegible] axis, were grown from methanol.

The space group was unequivocally established by Weissenberg and precession photographs.

Cell parameters and intensities were measured with a four-circle Hilger diffractometer using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å, ω–2θ scan). Integrated intensities were recorded for 3353 independent reflections. They were corrected for Lorentz and polarization effects but not for absorption (μ for Cu $K\alpha = 0{\cdot}72$ mm^{-1}).

The structure was solved by direct methods using *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). A large number of cycles of structure factor and Fourier calculations were necessary to find all the atoms. The oxygen atoms were identified with the help of chemical and structural considerations. Refinement of atomic coordinates and individual isotropic thermal parameters for C and O atoms was carried out by a full-matrix least-squares method (program *SFLS*, Prewitt, 1967) on 3139 reflections for which $I > 2\sigma(I)$. In the last cycles of refinement, H atoms were included in calculated positions assuming C—H bond lengths of 1·087 Å. All were given the same isotropic temperature factor $B = 4{\cdot}0$ Å^2. A Cruickshank (1961) type of weighting scheme was used. The final value of the conventional discrepancy factor R is 0·108. We could not carry out further refinement with anisotropic thermal parameters: the large number of variables would have involved

much computing time and expense. Our final positional and thermal parameters are listed in Table 1.*

Discussion

Our structural results indicate that acetylated napoleogenin is a pentacyclic oleanene-type triterpene of the β-amyrin series with a 3,4-di-*o*-angelyl-6-deoxy-β-glucopyranosyl group located on the *E* ring at C(21). Moreover, in the triterpene nucleus, a geminal dimethyl group is situated at C(20) and four other methyl groups at C(4), C(8), C(10) and C(14). Acetyl groups are located at C(3), C(16) and C(22) while two acetoxymethyl groups are found at C(4) and C(17). We deduced that acetylated napoleogenin should be formulated as 21β-(2-*O*-acetyl-3,4-di-*O*-angelyl-6-deoxy-β-glucopyranosyloxy)-3β,16α,22α,24,28-pentaacetoxyolean-12-ene. The numbering of the atoms is illustrated in Fig. 1. The molecular conformation is shown in Fig. 2, a stereodrawing produced by the program *PLUTO* (Crystallographic Data Files, 1979). Bond lengths and angles are listed in Tables 2 and 3.

* Lists of structure factors and hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35161 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *with standard deviations in parentheses*

(i) Triterpene nucleus		(ii) Extranuclear	
C(1)–C(2)	1·54 (2)	C(3)–O(1)	1·47 (2)
C(1)–C(10)	1·60 (2)	C(4)–C(23)	1·56 (2)
C(2)–C(3)	1·51 (2)	C(4)–C(24)	1·51 (2)
C(3)–C(4)	1·54 (2)	C(8)–C(26)	1·51 (2)
C(4)–C(5)	1·54 (2)	C(10)–C(25)	1·54 (2)
C(5)–C(6)	1·52 (2)	C(14)–C(27)	1·56 (2)
C(5)–C(10)	1·58 (2)	C(16)–O(5)	1·48 (1)
C(6)–C(7)	1·53 (2)	C(17)–C(28)	1·54 (2)
C(7)–C(8)	1·56 (2)	C(20)–C(29)	1·54 (2)
C(8)–C(9)	1·56 (2)	C(20)–C(30)	1·52 (2)
C(8)–C(14)	1·59 (2)	C(21)–O(11)	1·46 (1)
C(9)–C(10)	1·59 (2)	C(22)–O(9)	1·45 (2)
C(9)–C(11)	1·51 (2)	C(31)–O(1)	1·40 (2)
C(11)–C(12)	1·51 (2)	C(31)=O(2)	1·11 (2)
C(12)=C(13)	1·37 (2)	C(31)–C(32)	1·50 (3)
C(13)–C(14)	1·50 (2)	C(33)–O(3)	1·34 (2)
C(13)–C(18)	1·53 (2)	C(33)=O(4)	1·27 (2)
C(14)–C(15)	1·52 (2)	C(33)–C(34)	1·42 (3)
C(15)–C(16)	1·56 (2)	C(35)–O(5)	1·34 (2)
C(16)–C(17)	1·52 (2)	C(35)=O(6)	1·21 (2)
C(17)–C(18)	1·54 (2)	C(35)–C(36)	1·45 (3)
C(17)–C(22)	1·58 (2)	C(37)–O(7)	1·31 (2)
C(18)–C(19)	1·53 (2)	C(37)=O(8)	1·30 (3)
C(19)–C(20)	1·54 (2)	C(37)–C(38)	1·46 (3)
C(20)–C(21)	1·56 (2)	C(39)–O(9)	1·40 (2)
C(21)–C(22)	1·50 (2)	C(39)=O(10)	1·08 (2)
		C(39)–C(40)	1·55 (3)
(iii) Glucopyranosyl moiety			
C(1′)–O(11)	1·38 (1)	C(7′)–C(8′)	1·54 (2)
C(1′)–O(1′)	1·42 (2)	C(7″)–O(2″)	1·38 (2)
C(1′)–C(2′)	1·51 (2)	C(7″)=O(3″)	1·16 (2)
C(2′)–O(4′)	1·42 (1)	C(7″)–C(8″)	1·56 (3)
C(2′)–C(3′)	1·55 (2)	C(8′)–C(11′)	1·53 (3)
C(3′)–O(2″)	1·45 (1)	C(8′)=C(9′)	1·38 (3)
C(3′)–C(4′)	1·48 (2)	C(8″)–C(11″)	1·56 (3)
C(4′)–O(2′)	1·48 (1)	C(8″)=C(9″)	1·15 (3)
C(4′)–C(5′)	1·57 (2)	C(9′)–C(10′)	1·53 (2)
C(5′)–O(1′)	1·41 (1)	C(9″)–C(10″)	1·53 (2)
C(5′)–C(6′)	1·54 (2)	C(12′)–O(4′)	1·34 (2)
C(7′)–O(2′)	1·34 (2)	C(12′)=O(5′)	1·21 (2)
C(7′)=O(3′)	1·20 (2)	C(12′)–C(13′)	1·52 (3)

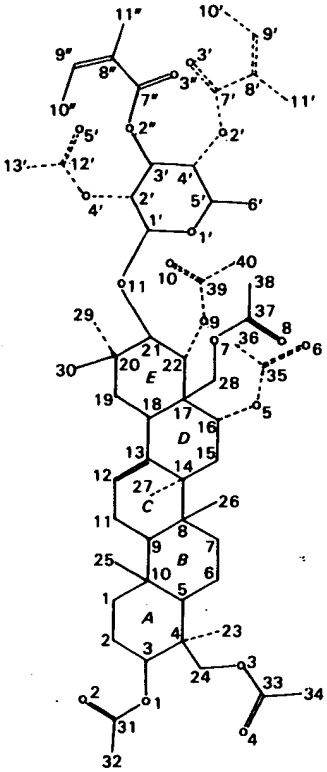

Fig. 1. Numbering of atoms in acetylated napoleogenin.

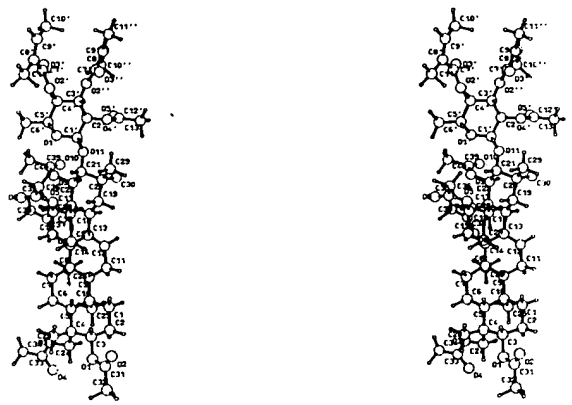

Fig. 2. Stereoscopic drawing of the molecule.

Table 3. *Bond angles* (°) *with standard deviations in parentheses*

(i) Triterpene nucleus			
C(2)–C(1)–C(10)	111 (1)	C(12)=C(13)–C(18)	115 (1)
C(1)–C(2)–C(3)	109 (1)	C(14)–C(13)–C(18)	124 (1)
C(2)–C(3)–C(4)	117 (1)	C(8)–C(14)–C(13)	110 (1)
C(2)–C(3)–O(1)	107 (1)	C(8)–C(14)–C(15)	110 (1)
C(4)–C(3)–O(1)	108 (1)	C(8)–C(14)–C(27)	112 (1)
C(3)–C(4)–C(5)	106 (1)	C(13)–C(14)–C(15)	110 (1)
C(3)–C(4)–C(23)	109 (1)	C(13)–C(14)–C(27)	106 (1)
C(3)–C(4)–C(24)	108 (1)	C(15)–C(14)–C(27)	109 (1)
C(5)–C(4)–C(23)	107 (1)	C(14)–C(15)–C(16)	118 (1)
C(5)–C(4)–C(24)	117 (1)	C(15)–C(16)–C(17)	113 (1)
C(23)–C(4)–C(24)	108 (1)	C(15)–C(16)–O(5)	108·0 (9)
C(4)–C(5)–C(6)	117 (1)	C(17)–C(16)–O(5)	107 (1)
C(4)–C(5)–C(10)	116 (1)	C(16)–C(17)–C(18)	114 (1)
C(6)–C(5)–C(10)	108 (1)	C(16)–C(17)–C(22)	113 (1)
C(5)–C(6)–C(7)	110 (1)	C(16)–C(17)–C(28)	107 (1)
C(6)–C(7)–C(8)	114 (1)	C(18)–C(17)–C(22)	110 (1)
C(7)–C(8)–C(9)	109 (1)	C(18)–C(17)–C(28)	105 (1)
C(7)–C(8)–C(14)	110 (1)	C(22)–C(17)–C(28)	109 (1)
C(7)–C(8)–C(26)	110 (1)	C(13)–C(18)–C(17)	112 (1)
C(9)–C(8)–C(14)	107·3 (9)	C(13)–C(18)–C(19)	112 (1)
C(9)–C(8)–C(26)	111 (1)	C(17)–C(18)–C(19)	113 (1)
C(14)–C(8)–C(26)	110 (1)	C(18)–C(19)–C(20)	115 (1)
C(8)–C(9)–C(10)	115 (1)	C(19)–C(20)–C(21)	104 (1)
C(8)–C(9)–C(11)	111 (1)	C(19)–C(20)–C(29)	108 (1)
C(10)–C(9)–C(11)	112 (1)	C(19)–C(20)–C(30)	112 (1)
C(1)–C(10)–C(5)	108 (1)	C(21)–C(20)–C(29)	110 (1)
C(1)–C(10)–C(9)	104 (1)	C(21)–C(20)–C(30)	114 (1)
C(1)–C(10)–C(25)	107 (1)	C(29)–C(20)–C(30)	109 (1)
C(5)–C(10)–C(9)	106 (1)	C(20)–C(21)–C(22)	112 (1)
C(5)–C(10)–C(25)	116 (1)	C(20)–C(21)–O(11)	108·5 (9)
C(9)–C(10)–C(25)	115 (1)	C(22)–C(21)–O(11)	106·4 (9)
C(9)–C(11)–C(12)	114 (1)	C(17)–C(22)–C(21)	117 (1)
C(11)–C(12)=C(13)	125 (1)	C(17)–C(22)–O(9)	107·2 (9)
C(12)=C(13)–C(14)	121 (1)	C(21)–C(22)–O(9)	105·4 (9)
(ii) Extranuclear			
C(24)–O(3)–C(24)	123 (1)	O(4)=C(33)–C(34)	131 (2)
C(16)–O(5)–C(35)	121 (1)	O(5)–C(35)=O(6)	120 (1)
C(28)–O(7)–C(28)	119 (1)	O(5)–C(35)–C(36)	111 (1)
C(21)–O(11)–C(1′)	116·3 (9)	O(6)=C(35)–C(36)	129 (2)
C(4)–C(24)–O(3)	109 (1)	O(7)–C(37)=O(8)	116 (2)
C(17)–C(28)–O(7)	109 (1)	O(7)–C(37)–C(38)	113 (2)
O(1)–C(31)=O(2)	125 (2)	O(8)=C(37)–C(38)	129 (2)
O(1)–C(31)–C(32)	106 (2)	O(9)–C(39)=O(10)	125 (2)
O(2)=C(31)=C(32)	128 (2)	O(9)–C(39)–C(40)	104 (1)
O(3)–C(33)=O(4)	115 (2)	O(10)=C(39)–C(40)	130 (2)
O(3)–C(33)–C(34)	114 (2)		
(iii) Glucopyranosyl moiety			
O(11)–C(1′)–C(2′)	110 (1)	C(2′)–O(4′)–C(12′)	117 (1)
O(11)–C(1′)–O(1′)	108·8 (9)	O(2′)–C(7′)–O(3′)	119 (2)
C(2′)–C(1′)–O(1′)	109 (1)	O(2′)–C(7′)–C(8′)	109 (1)
C(1′)–C(2′)–C(3′)	110 (1)	O(3′)–C(7′)–C(8′)	132 (2)
C(1′)–C(2′)–C(4′)	110 (1)	O(2″)–C(7″)–O(3″)	126 (2)
C(3′)–C(2′)–O(4′)	106·3 (9)	O(2″)–C(7″)–C(8″)	110 (1)
C(2′)–C(3′)–C(4′)	110 (1)	O(3″)–C(7″)–C(8″)	124 (2)
C(2′)–C(3′)–O(2″)	104 (1)	C(7′)–C(8′)=C(9′)	112 (2)
C(4′)–C(3′)–O(2′)	108 (1)	C(7′)–C(8′)–C(11′)	118 (2)
C(3′)–C(4′)–C(5′)	112 (1)	C(9′)=C(8′)–C(11′)	130 (2)
C(3′)–C(4′)–O(2′)	108 (1)	C(7″)–C(8″)=C(9″)	129 (2)
O(2′)–C(4′)–C(5′)	104 (1)	C(7″)–C(8″)–C(11″)	106 (2)
C(4′)–C(5′)–C(6′)	113 (1)	C(9″)=C(8″)–C(11″)	125 (2)
C(4′)–C(5′)–O(1′)	108 (1)	C(8′)=C(9′)–C(10′)	134 (2)
C(8′)–C(5′)–O(1′)	108 (1)	C(8″)=C(9″)–C(10″)	132 (2)
C(1′)–O(1′)–C(1′)	111·6 (9)	O(4′)–C(12′)=O(5′)	125 (1)
C(4′)–O(2′)–C(7′)	120 (1)	O(4′)–C(12′)–C(13′)	112 (1)
C(3′)–O(2″)–C(7″)	114 (1)	O(5′)=C(12′)–C(13′)	123 (2)

In the triterpene skeleton, several C–C bonds [C(1)–C(10); C(5)–C(10); C(8)–C(14); C(9)–C(10); C(17)–C(22)] deviate from the mean value of 1·54 Å. it seems significant that all these long C–C bonds are attached to at least one of the fully substituted carbon atoms [C(8), C(10), C(14) and C(17)]. Several C–C–C angles also deviate from the accepted value of 109·3°. The degrees of substitution of the carbon atoms and long-range steric strain in the structure (s below) seem to be responsible for these deviations.

The C(12)–C(13) bond [1·37 (2) Å] is shorter th the remainder of the ring-system bonds and corr sponds to the expected location of the double bond oleanene triterpenes.

In Table 4, the conformation of the ring system analyzed in terms of the least-squares planes an interplanar angles. The equations of the least-squar planes were calculated by the method of Schomake Waser, Marsh & Bergman (1959). The torsional angl in the ring system are given in Table 5(i). From Tabl 4 and 5, it is clear that the rings *A*, *B*, *D* and *E* take

Table 4. *Least-squares planes*

(*a*) Equations of the planes

Plane *A* C(1), C(2), C(3), C(4), C(5), C(10)
$-0{\cdot}8682x - 0{\cdot}4203y - 0{\cdot}2637z + 9{\cdot}6570 = 0$

Plane *B* C(5), C(6), C(7), C(8), C(9), C(10)
$-0{\cdot}8343x - 0{\cdot}5346y + 0{\cdot}1344z + 9{\cdot}2884 = 0$

Plane *C* C(8), C(9), C(11), C(12), C(13), C(14)
$-0{\cdot}7409x - 0{\cdot}6612y + 0{\cdot}1178z + 7{\cdot}8474 = 0$

Plane *D* C(13), C(14), C(15), C(16), C(17), C(18)
$-0{\cdot}8455x - 0{\cdot}5273y - 0{\cdot}0838z + 10{\cdot}3836 = 0$

Plane *E* C(17), C(18), C(19), C(20), C(21), C(22)
$-0{\cdot}8856x + 0{\cdot}1556y + 0{\cdot}4376z + 9{\cdot}1570 = 0$

Plane *F* C(21), O(11), C(1′)
$0{\cdot}0951x - 0{\cdot}9953y - 0{\cdot}0203z - 2{\cdot}6655 = 0$

Plane *G* C(1′), C(2′), C(3′), C(4′), C(5′), O(1′)
$-0{\cdot}4992x - 0{\cdot}6567y + 0{\cdot}5653z + 1{\cdot}0736 = 0$

(*b*) Deviations (Å) from the least-squares planes

Plane *A*		Plane *B*		Plane *C*	
C(1)	−0·24 (1)	C(5)	−0·50 (1)	C(8)	0·38 (1)
C(2)	0·25 (2)	C(6)	0·15 (1)	C(9)	−0·29 (1)
C(3)	−0·24 (2)	C(7)	−0·15 (1)	C(11)	0·04 (2)
C(4)	0·22 (1)	C(8)	0·39 (1)	C(12)	0·09 (1)
C(5)	−0·23 (1)	C(9)	−0·08 (1)	C(13)	−0·004 (1)
C(10)	0·23 (1)	C(10)	0·19 (1)	C(14)	−0·23 (1)
O(1)	0·26 (1)	C(25)	1·66 (2)	C(26)	1·88 (1)
C(23)	−0·56 (2)	C(26)	1·89 (1)	C(27)	−1·77 (1)
C(24)	1·69 (1)				
C(25)	1·75 (2)				

Plane *D*		Plane *E*		Plane *G*	
C(13)	0·11 (1)	C(17)	−0·13 (1)	C(1′)	−0·26 (1)
C(14)	−0·12 (1)	C(18)	0·18 (1)	C(2′)	0·22 (1)
C(15)	0·17 (1)	C(19)	−0·27 (1)	C(3′)	−0·21 (1)
C(16)	−0·23 (1)	C(20)	0·30 (1)	C(4′)	0·21 (1)
C(17)	0·21 (1)	C(21)	−0·26 (1)	C(5′)	−0·24 (1)
C(18)	−0·16 (1)	C(22)	0·19 (1)	O(1′)	0·28 (1)
C(27)	−1·63 (1)	C(28)	0·83 (1)	O(11)	0·15 (1)
O(5)	−1·71 (1)	C(29)	−0·29 (1)	O(4′)	−0·40 (1)
C(28)	1·75 (1)	C(30)	1·81 (1)	O(2″)	0·54 (1)
		O(11)	0·28 (1)	O(2′)	−0·52 (1)
		O(9)	−0·52 (1)	C(6′)	0·28 (2)

(*c*) Interplanar angles (°)

A/*B*	156·0 (4)	*D*/*E*	129·1 (3)
B/*C*	170·9 (4)	*E*/*F*	75·6 (2)
C/*D*	164·9 (4)	*F*/*G*	126·5 (3)

Table 5. *Torsional angles* (°)

Triterpene nucleus		C(8)–C(9)–C(11)–C(12)	37·0 (1)	(ii) Glucopyranosyl ring	
C(1)–C(2)–C(3)	55·6 (2)	C(9)–C(11)–C(12)–C(13)	6·5 (1)	O(1′)–C(1′)–C(2′)–C(3′)	58·6 (2)
C(2)–C(3)–C(4)	58·1 (2)	C(11)–C(12)–C(13)–C(14)	2·0 (1)	C(2′)–C(1′)–O(1′)–C(5′)	−67·1 (3)
C(3)–C(4)–C(5)	54·8 (2)	C(12)–C(13)–C(14)–C(15)	−150·0 (3)	C(1′)–C(2′)–C(3′)–C(4′)	−54·2 (2)
C(4)–C(5)–C(10)	−53·6 (2)	C(18)–C(13)–C(14)–C(15)	32·3 (2)	C(2′)–C(3′)–C(4′)–C(5′)	−53·0 (2)
C(5)–C(6)–C(7)	64·9 (2)	C(14)–C(13)–C(18)–C(17)	−35·8 (2)	C(3′)–C(4′)–C(5′)–O(1′)	−56·9 (2)
C(5)–C(10)–C(9)	−165·5 (4)	C(13)–C(14)–C(15)–C(16)	37·4 (2)	C(4′)–C(5′)–O(1′)–C(1′)	63·8 (3)
C(5)–C(10)–C(1)	171·9 (3)	C(14)–C(15)–C(16)–C(17)	48·5 (3)		
C(5)–C(10)–C(9)	61·1 (2)	C(15)–C(16)–C(17)–C(18)	50·4 (3)	(iii) Angelyl groups	
C(6)–C(7)–C(8)	60·3 (2)	C(16)–C(17)–C(18)–C(13)	42·9 (3)	C(4′)–C(3′)–O(2″)–C(7″)	113·4 (3)
C(7)–C(8)–C(9)	50·4 (2)	C(16)–C(17)–C(18)–C(19)	83·5 (3)	O(2″)–C(7″)–C(8″)–C(9″)	−11·60 (2)
C(8)–C(9)–C(10)	50·5 (2)	C(22)–C(17)–C(18)–C(13)	−169·1 (3)	O(3″)–C(7″)–C(8″)–C(11″)	−19·54 (2)
C(8)–C(9)–C(11)	179·7 (4)	C(22)–C(17)–C(18)–C(19)	42·6 (3)	C(11″)–C(8″)–C(9″)–C(10″)	171·14 (3)
C(8)–C(9)–C(10)	169·1 (3)	C(18)–C(17)–C(22)–C(21)	43·1 (2)	C(3′)–C(4′)–O(2′)–C(7′)	106·8 (4)
C(8)–C(9)–C(11)	−61·7 (2)	C(17)–C(18)–C(19)–C(20)	56·7 (3)	O(2′)–C(7′)–C(8′)–C(9′)	144·3 (4)
C(8)–C(14)–C(13)	56·3 (1)	C(18)–C(19)–C(20)–C(21)	−62·2 (3)	O(3′)–C(7′)–C(8′)–C(11′)	149·1 (3)
C(9)–C(10)–C(1)	61·5 (2)	C(19)–C(20)–C(21)–C(22)	59·6 (3)	C(11′)–C(8′)–C(9′)–C(10′)	174·6 (4)

air conformation while the *C* ring adopts a half-chair formation as a result of the double bond between (12) and C(13). The junctions of the *A*/*B* and *B*/*C* s are in the *trans* form while that between the *D* and rings is *cis*. The rings *B*, *D* and *E* are significantly orted as is the whole molecular skeleton. These tortions seem to be caused mainly by the inter- ions between the bulky axial groups [at C(4), C(8), (10) on one hand and at C(14) and C(16) on the her] which push each other away in order to release repulsive forces. Actually, the non-bonded distances tween 1,3 diaxial groups are larger than the expected nes in non-distorted rings. We have reported these tances in Table 6. In a regular chair-form six- mbered ring, the non-bonded distances between 1,3 ial groups would be 2·52 Å. These distances are e increased to, for example, 3·27 (2) Å [C(24) C(25)].

The distortion of ring *C* from a regular half-chair nformation may be due to the degree of substitution C(8) and C(14). Also resulting from 1,3 diaxial eraction is the distortion of the whole molecule. As own by the angles between the mean planes of the s *A*, *B*, *C* and *D*, the triterpene skeleton is convex wards the axial groups C(24), C(25), C(26) and (28). On the other hand there is twisting between s *E* and *D* about the long direction of the molecule. e reason for this distortion appears to be the *cis D*/*E* junction and the steric effect of the three bulky acetate groups situated at C(16), C(17) and (22). A similar conformation of the triterpenic leus has been previously observed in gymnema- m by Hoge & Nordman (1974).

The glucopyranosyl ring has an almost regular chair nformation with all the substituent groups in atorial positions. The bond distances agree with the es reported for β-D-glucose (Chu & Jeffrey, 1968) with one exception: the C(3′)–C(4′) bond is significantly shorter in comparison with the accepted value of 1·54 Å. Moreover, the two angles C(2′)–C(3′)–O(2″) and C(5′)–C(4′)–O(2′) differ from the tetrahedral angle of 109·5°. Steric strain resulting from the two long angelyl side chains situated at C(3′) and C(4′) could be responsible for these unusual values. Indeed, these angelyl groups, in order to overcome any overlapping, are rotated with respect to each other by

Table 6. *Some non-bonded distances* (Å) *between* 1,3 *diaxial groups*

C(24)---C(25)	3·27 (2)
C(25)---C(26)	3·20 (2)
C(27)---O(5)	3·06 (2)
O(5)---O(9)	2·97 (1)

Table 7. *Shortest intermolecular distances* (Å) *with standard deviations in parentheses*

Key to symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*):

(i) $\bar{x}+1, \frac{1}{2}+y, \bar{z}$	(iv) $\bar{x}+1, \frac{1}{2}+y, \bar{z}+1$
(ii) $\bar{x}+2, \frac{1}{2}+y, \bar{z}+1$	(v) $x, y-1, z$
(iii) $x, y, z+1$	(vi) $\bar{x}+2, \frac{1}{2}+y, \bar{z}+2$.

C(2)···O(8^{i})	3·56 (3)	C(30)···O(2^{iii})	3·63 (2)
C(7)···O(3″^{ii})	3·69 (2)	C(32)···O(4^{iv})	3·10 (3)
C(12)···C(33^{i})	3·60 (2)	C(34)···O(2^{v})	3·30 (3)
C(12)···O(4^{i})	3·35 (2)	C(36)···C(40^{ii})	3·57 (3)
C(23)···O(10^{iii})	3·60 (2)	C(38)···O(4^{i})	3·58 (3)
C(23)···O(5′^{iii})	3·56 (2)	O(1)···O(8^{i})	3·36 (2)
C(24)···O(8^{i})	3·52 (3)	O(6)···C(3′^{ii})	3·46 (2)
C(29)···C(36^{ii})	3·61 (3)	O(6)···C(5′^{ii})	3·68 (2)
C(30)···C(31^{iii})	3·55 (2)	C(13′)···O(3′^{vi})	3·54 (3)

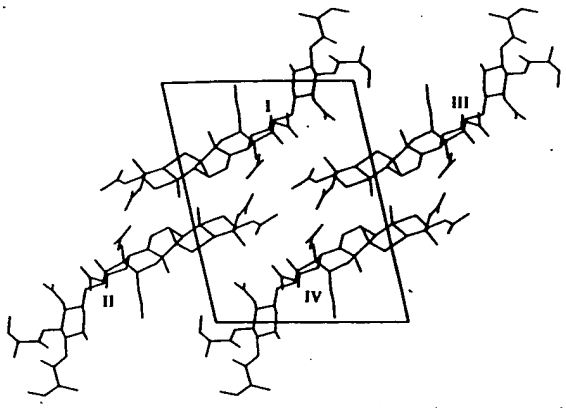

Fig. 3. Projection of the acetylated napoleogenin structure along the *b* axis. The positions of the molecules are; (I) at x, y, z; (II) at $\bar{x}+1, \frac{1}{2}+y, z$; (III) at $x, y, z+1$; (IV) at $x+1, \frac{1}{2}+y, \bar{z}+1$ with x, y and z coordinates given in Table 1.

about 180° about the C(7′)—C(8′) bond [the corresponding torsional angles are reported in Table 5(iii)].

One should also notice that in both angelyl and acetyl groups, the accuracy of bond lengths and valency angles is highly restricted by a large thermal motion of the end-chain atoms.

A packing diagram of the crystal structure viewed along the *b* axis is shown in Fig. 3. The intermolecular distances less than 3·7 Å are reported in Table 7. There is no abnormal feature in the packing, which appears to be dictated mainly by close van der Waals cont between the molecules.

The authors wish to thank Professors J. Touss and A. Van de Vorst for their interest in this work Mr M. Vermeire for technical assistance. Crystals acetylated napoleogenin were provided by Laboratoire de Chimie Organique of Professor R. H

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The Structure of 2-Amino-5-nitrophenol: a Comparison with 2-Aminophenol

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(*Received* 23 *October* 1979; *accepted* 11 *February* 1980)

Abstract

The crystal structure of 2-amino-5-nitrophenol has been determined from visually estimated Cu $K\alpha$ data, and refined to an R value of 0·072 for 1138 non-zero reflexions. The crystals are monoclinic, $P2_1/c$, with $a = 8{\cdot}49\,(1)$, $b = 10{\cdot}34\,(1)$, $c = 8{\cdot}05\,(1)$ Å, $\beta = 113{\cdot}1\,(1)°$ and $Z = 4$. The molecules, related by a glide plane, are held together by O—H···NH_2 hydrogen bonds [O···N 2·801 (3), H···N 1·89 (4) Å, O—H···N 174 (3)°] to form a ribbon along **c**. The ribbons are held together by dipole–dipole interactions between the molecules related by $\bar{1}$, as found c monly in mononitrophenols. The morphotropism mononitrophenols and aminophenols is discussed.

Introduction

As part of a programme of studies on the crystal molecular structures of phenols (Kagawa, Ka Kashino & Haisa, 1976) and the systemization organic crystals (Haisa, 1978), the structure amino-5-nitrophenol has been determined in orde

0567-7408/80/071598-04$01.00